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# Electrochemical intercalation of bis(fluorosulfonyl)amide anions into graphite from aqueous solutions

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ABSTRACT

Graphite intercalation compounds of bis(fluorosulfonyl)amide (FSA-GICs) are electrochemically synthesized in a highly concentrated aqueous solution. While only water decomposition occurs at the graphite electrode in a dilute aqueous solution (1 mol $kg^{-1}$ NaFSA), redox peaks clearly appear in a highly concentrated aqueous solution (19 mol $kg^{-1}$ NaFSA). Under the application of a constant current, the electrode potential reaches 1.7 V (*vs.* Ag/AgCl), which is far beyond the upper limit of the potential window, in 19 mol $kg^{-1}$ NaFSA aq., and the formation of FSA-GIC is confirmed by X-ray diffraction patterns. Acceptor-type GICs using organic anions are observed for the first time in highly concentrated aqueous solutions of NaFSA.

## 1. Introduction

Ions and molecules are intercalated into graphite by both chemical and electrochemical methods, and graphite intercalation compounds (GICs) are formed. GICs have been studied as potential materials for many applications [1]. For example, electrochemical $Li^+$ intercalation is seen as a reaction at the negative electrode in lithium-ion batteries [2], and GICs are also used to produce graphene oxides (GOs) as a mother material for exfoliated graphite and graphite sheets [3]. Since GOs can be potentially used in electronics, conductive films, electrode materials, and composites, numerous studies have been performed to explore an efficient route for the mass production of GICs [4].

Conventionally, a solution of sulfonic acid is used to form a precursor GIC ($C_x^+HSO_4^-\cdot 2.5H_2SO_4$) for GO production [5]. The solution of sulfonic acid should be concentrated to at least 50 wt% $H_2SO_4$; otherwise, water decomposition (*i.e.*, oxygen evolution) will hinder the formation of GICs. Such strong acid solutions, however, require post-treatment for neutralization, which is a high-maintenance process and could damage the surface of graphite. On the other hand, while non-aqueous electrolyte solutions are also used for the formation of GICs [6–9], they are very expensive and environmental problems should be considered. Therefore, there is a great need for a process for the formation of GICs using environmentally friendly aqueous solutions.

There are serious concerns regarding the stability of aqueous solutions at high electrode potentials. Generally, during the formation of GICs, the electrode potential must be above the upper limit of the potential window of water. Recently, highly concentrated aqueous electrolyte solutions with alkali metal cation-organic anion salts with a wide potential window have been reported for aqueous lithium-ion batteries and aqueous sodium-ion batteries [10–12]. For example, large amounts of lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) and sodium bis(fluorosulfonyl)amide (NaFSA) can be dissolved in water at room temperature. These concentrated aqueous electrolytes are neutral, and the electrochemical potential window of neutral aqueous electrolyte solutions is expanded [13]. In addition, a high concentration of anion is favorable for anion intercalation, since the standard potential of anion intercalation/de-intercalation should be shifted negatively with an increase in the concentration, according to the Nernst equation. Therefore, highly concentrated aqueous solutions are promising candidates as electrolytes, in which GICs can be formed.

In this study, the intercalation of bis(fluorosulfonyl)amide (FSA) anion into graphite is investigated using highly concentrated aqueous solutions of NaFSA. This is because FSA salts are known to be much more highly soluble than other anion salts owing to the weaker interaction between cations and FSA anions [9,14]. Previously, we reported the intercalation of FSA anion in non-aqueous solutions [9]. FSA-GIC was formed at a high potential (5 V *vs.* $Li^+$/Li), which is far above the potential window of water. Therefore, the potential window of aqueous solutions should be expanded to suppress the oxygen evolution reaction. Concentrated NaFSA aqueous solutions are neutral, relatively safer and low toxic, compared with acid solutions, organic electrolytes, and ionic liquids. To the best of our knowledge, there is no previous report about the intercalation of organic anions into graphite using aqueous solutions.

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## 2. Experimental

A three-electrode cell was used for electrochemical measurements. The working electrode consisted of a highly oriented pyrolytic graphite (HOPG, Momentive) wrapped in a platinum mesh, and the counter electrode and reference electrode were a platinum mesh and Ag/AgCl electrode. HOPGs were cut into a slab measuring *ca.* 5 mm × 5 mm × 0.5 mm with a weight of *ca.* 15 mg. Electrolyte solutions consisted of aqueous solutions of 1 and 19 mol $kg^{-1}$ NaFSA. The aqueous solution in this study was almost saturated at 19 mol $kg^{-1}$ NaFSA at ambient temperature. Cyclic voltammetry was conducted between the open circuit potential (OCP) and 1.7 V (*vs.* Ag/AgCl), and the scan rate was set at 1 mV $s^{-1}$. Chronopotentiometry was also conducted with various constant currents in a potential range of 0.2 to 1.7 V. Notably, positive currents (*i.e.*, oxidation) correspond to the intercalation of anions and negative currents (*i.e.*, reduction) correspond to the de-intercalation of anions. Applied currents are normalized by the weight of HOPG electrodes. X-ray diffraction (XRD) measurement and Raman spectroscopy were used to investigate the structural changes of graphite by applying currents. XRD patterns were taken using CuKα radiation over a 2$\theta$ range of 5–60°. Raman spectroscopy was carried out using a 515 nm laser (100 mW). All electrochemical measurements were carried out using an HSV-100 (Hokuto-Denko) and HJ1001SD8 (Hokuto-Denko).

## 3. Results and discussion

Fig. 1 shows the CVs of HOPG electrodes in aqueous solutions of 1 and 19 mol $kg^{-1}$ NaFSA. While large oxidative currents were observed at around 1.5 V in 1 mol $kg^{-1}$ NaFSA aq., oxidative currents were strongly suppressed in 19 mol $kg^{-1}$ NaFSA. Possible oxidation reactions at high potentials include $FSA^-$ intercalation and water decomposition. With various kinds of salts, water decomposition is suppressed in aqueous solutions with low water concentrations [13]. The water concentration of 19 mol $kg^{-1}$ NaFSA aq. was 21 mol $dm^{-3}$, and this relatively lower value caused the suppression of water decomposition [13]. The molar ratio of NaFSA/water for 1 mol $kg^{-1}$ NaFSA aq. and 19 mol $kg^{-1}$ NaFSA aq. were *ca.* 1/56 and 1/3, respectively. In addition, Raman spectrum of 19 mol $kg^{-1}$ NaFSA aq. was measured to clarify the solution structure. As shown in Fig. S1 (Supporting information), the OH stretching band of water in 19 mol $kg^{-1}$ NaFSA aq. was relatively narrow like the Raman spectrum of "water-in-salt" solution (21 mol $kg^{-1}$ LiTFSA aq.) [11], indicating that free water molecules decreased owing to the high concentration. As a result, the suppression of water decomposition resulted in low oxidative currents. In addition, reductive currents were clearly observed at around 1.5 V. Such oxidative and reductive currents imply that the intercalation/de-intercalation of $FSA^-$ proceeded on graphite in 19 mol $kg^{-1}$ NaFSA aq. In a non-aqueous solution, the intercalation/de-intercalation of $FSA^-$ occurred when the concentration of $FSA^-$ was 1 mol $dm^{-3}$ (LiFSA) [9]. Therefore, we consider that the formation of FSA-GIC occurred, even in 1 mol $kg^{-1}$ NaFSA aq., but it immediately vanished by reacting with water. In contrast, formed FSA-GIC was successfully retained in 19 mol $kg^{-1}$ NaFSA aq., where water molecules were inactive so that the de-intercalation of $FSA^-$ was also observed.

Under the application of constant currents, the potential curves of HOPG electrodes as a function of electric charge ($Q$) in aqueous solutions of 1 and 19 mol $kg^{-1}$ NaFSA are shown in Fig. 2. When we applied +10 mA $g^{-1}$ in 1 mol $kg^{-1}$ NaFSA aq., the potential did not reach the cut-off potential of 1.7 V and stayed at about 1.4 V. As in Fig. 1(a), water decomposition mainly occurred on the HOPG electrode and showed a constant potential. In contrast, the potential rose to 1.7 V in 19 mol $kg^{-1}$ NaFSA aq. under the application of +10 mA $g^{-1}$. To form FSA-GIC, a high electrode potential is necessary to intercalate $FSA^-$ into graphite. In the non-aqueous solution, FSA-GIC was formed at about 5 V (*vs.* $Li^+$/Li), which corresponds to 1.7 V (*vs.* Ag/AgCl), but

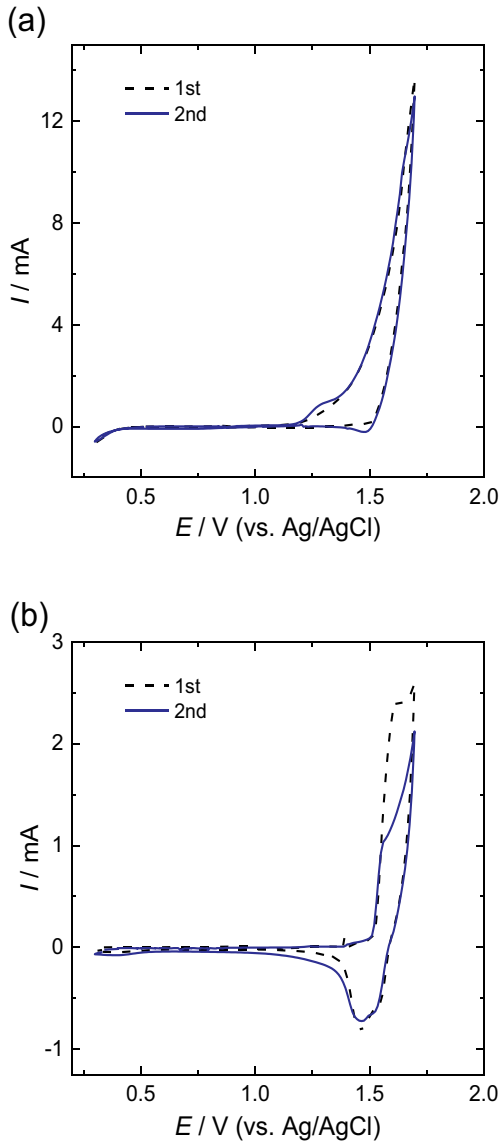


**Fig. 1.** Cyclic voltammograms of HOPG electrodes in aqueous solutions of (a) 1 mol $kg^{-1}$ NaFSA and (b) 19 mol $kg^{-1}$ NaFSA. Scan rate: 1 mV $s^{-1}$.

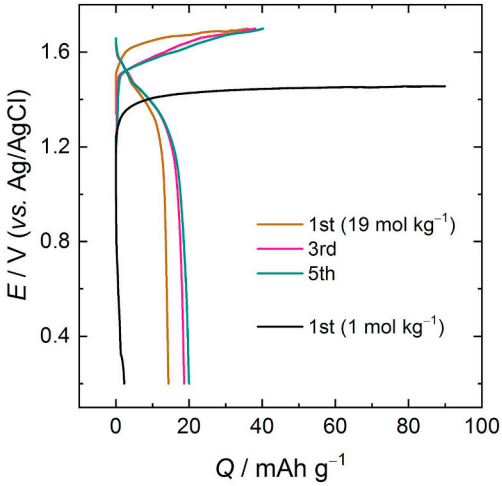


**Fig. 2.** Polarization curves of HOPG electrodes in aqueous solution of 1 and 19 mol $kg^{-1}$ NaFSA. Constant current: ± 10 mA $g^{-1}$.

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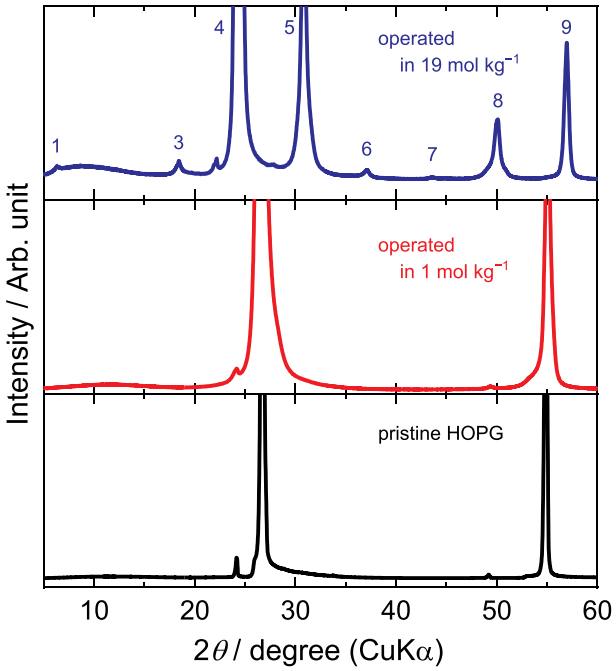


**Fig. 3.** XRD patterns of HOPG electrodes; pristine, oxidized in 1 mol $kg^{-1}$ NaFSA aq., and in 19 mol $kg^{-1}$ NaFSA aq. Numbers denote 00*l* diffractions.

such potential is far beyond the potential window of water [9]. Therefore, the concentrated aqueous solution (19 mol $kg^{-1}$ NaFSA) has an advantage to achieve a high electrode potential even using aqueous solutions. Furthermore, a reversible electric charge was observed in 19 mol $kg^{-1}$ NaFSA aq. under the application of −10 mA $g^{-1}$, implying that the de-intercalation of $FSA^-$ from GICs occurred during reduction. The reason for this reversible charge in 19 mol $kg^{-1}$ NaFSA aq. was not the difference between the conductivities of electrolyte solutions, but rather the difference between potential windows because the conductivity of 19 mol $kg^{-1}$ NaFSA aq. is higher than that of 1 mol $kg^{-1}$ NaFSA aq. [11].

To clarify the structural changes of HOPG after electrochemical polarization, XRD measurements and Raman spectroscopy were performed after a 2nd oxidation (+10 mA $g^{-1}$). Fig. 3 shows the XRD patterns of HOPG electrodes after oxidation, compared with pristine HOPG. No new peak was observed after oxidation in the normal aqueous solution (1 mol $kg^{-1}$ NaFSA), and therefore there was no change in the structure of graphite. In contrast, in 19 mol $kg^{-1}$ NaFSA aq., new peaks clearly appeared at $2\theta$ = 6.28, 18.4, 24.56, 30.84, 37.1, 43.58, 50.00, and 56.92° for oxidized HOPG, and the original peaks ($2\theta$ = 26.5 and 55°) of pristine HOPG disappeared. These new peaks were indexed with the same sandwich distance (0.78 nm) as FSA-GIC produced in the non-aqueous solutions [9], and are denoted by 00*l* in Fig. 3. A calculated repeating distance of 1.45 nm on the *c* axis is in agreement with the formation of stage 3 GIC: 0.78 nm + 0.335 nm × 2 = 1.45 nm. Hence, the formation of stage 3 FSA-GIC was confirmed in the aqueous solution with a high concentration of NaFSA. De-intercalation capacity of *ca.* 20 mAh $g^{-1}$ corresponding to $C_{112}FSA$ was almost the same as LiTFSA-organic solution system [15]. One possible explanation for such low capacity is the decline of the intercalation capacity by the co-intercalation with water molecules. Recently, the co-intercalation of organic solvents during anion intercalation in non-aqueous solutions was reported [16,17]. Co-intercalation with solvents can make the intercalation capacity smaller. Actually, the de-intercalation capacity of amide anion in organic electrolyte solutions (55 mAh $g^{-1}$) [17] were smaller than that in ionic liquid electrolytes (80 mAh $g^{-1}$) [15]. The de-intercalation capacity of 20 mAh $g^{-1}$ for stage 3 FSA-GIC, in this study, was consistent with the discharge capacity of 60 mAh $g^{-1}$ for stage 1

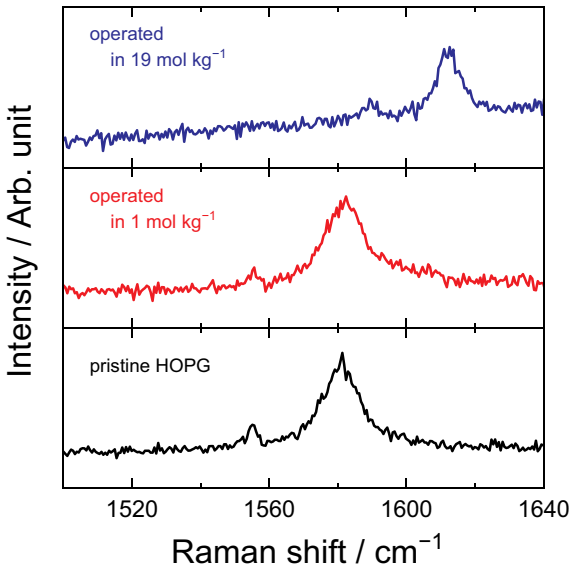


**Fig. 4.** Raman spectra of HOPG electrodes; pristine, oxidized in 1 mol $kg^{-1}$ NaFSA aq. and in 19 mol $kg^{-1}$ NaFSA aq.

FSA-GIC synthesized in 1 mol $dm^{-3}$ LiFSA organic solution [9]. To clarify whether co-intercalation occurred or not, further study is needed in the future.

Fig. 4 shows the Raman spectra of HOPG electrodes after oxidation, compared with pristine HOPG. The spectrum of pristine HOPG shows the G-band at *ca.* 1580 $cm^{-1}$ and the band at *ca.* 1555 $cm^{-1}$ derived from $O_2$, and the spectrum did not change after oxidation in 1 mol $kg^{-1}$ NaFSA aq. In contrast, the G-band became very weak and was slightly shifted, and the new band derived from GICs appeared at 1612 $cm^{-1}$ after oxidation in 19 mol $kg^{-1}$ NaFSA aq. Based on the intensity ratio of the G-band and new band, stage 2 and 3 FSA-GICs coexisted near the surface of HOPG.

In this study, stage 3 FSA-GIC was obtained inside the bulk of HOPG as the lowest-stage GIC. As already mentioned, we produced stage 1–2 FSA-GICs in non-aqueous solution by electrochemical oxidation [9]. Generally, much more energy (*i.e.*, higher potential) is required to produce lower-stage acceptor-type GICs, which contain anions as a guest. If the potential had been raised beyond 1.7 V, the formation of lower-stage FSA-GICs would be achieved. Water decomposition, however, is also accelerated at a potential higher than 1.7 V, dominates the oxidation current according to the Butler-Volmer equation. As a result, further lowering of the stage of FSA-GICs is inhibited by water decomposition. To produce stage 1–2 FSA-GICs in aqueous solutions, it will be necessary to explore other approaches for suppressing water decomposition, in addition to using concentrated solutions.

## 4. Conclusion

Electrochemical synthesis of FSA-GICs was performed in a highly concentrated aqueous electrolyte solution using NaFSA as an electrolyte salt. In cyclic voltammograms, only oxidative currents were observed in a dilute aqueous electrolyte, but large redox peaks at high potential appeared in a highly concentrated aqueous electrolyte, indicating the intercalation/de-intercalation of FSA anions. XRD patterns show the formation of stage 3 FSA-GICs in highly concentrated aqueous solutions, which is also confirmed by Raman spectroscopy. For the first time, acceptor-type GICs of organic anions were synthesized in aqueous solutions.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2019.01.015.

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## Conflicts of interest

There is no conflict of interest.

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